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(54) Title: METHOD FOR PRODUCING MOLYBDENUM-BISMUTH-IRON CONTAINING COMPOSITE OXIDE FLUID BED CATALYST

(54) 発明の名称: モリブデン－ビスマス－鉄含有複合酸化物流動層触媒の製法

(57) Abstract: A method for producing a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst for use in an ammoxidation of an organic compound, which comprises a step of subjecting a slurry containing raw materials of specific component elements to a concentration treatment at a temperature range of 50 to 120 ° C. The method can be employed for producing a catalyst which exhibits high activity and provides an objective ammoxidation product with a high yield, in good reproducibility.

(57) 要約:

本発明の目的の１つは、アンモ酸化反応に有用なモリブデン－ビスマス－鉄含有複合酸化物流動層触媒の製造において、高活性で、かつ目的とするアンモ酸化生成物を高収率で与える触媒を再現性良く製造する方法を提供することにある。この目的を達成するために、有機化合物のアンモ酸化反応に用いるモリブデン－ビスマス－鉄含有複合酸化物流動層触媒を製造するに際し、特定の成分元素の原料を含むスラリーを５０～１２０℃の温度範囲で濃縮処理する工程を含む方法を提供する。

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明細書

モリブデン－ビスマス－鉄含有複合酸化物流動層触媒の製法

技術分野

本発明は、モリブデン－ビスマス－鉄含有複合酸化物流動層触媒を製造する方法に関し、更に詳しくは種々の有機化合物のアンモ酸化反応に用いるモリブデン－ビスマス－鉄含有複合酸化物流動層触媒の製法に関する。

背景技術

オレフィンのアンモ酸化によるアンモ酸化生成物の製造に適する触媒として、種々の触媒が開示されている。特公昭３８－１７９６７号公報にはモリブデン、ビスマス及び鉄を含む酸化物触媒が、特公昭３８－１９１１１号公報には鉄及びアンチモンを含む酸化物触媒が示されている。その後これらの触媒の改良が精力的に続けられ、例えば特公昭５１－３３８８８号公報、特開昭５５－５６８３９号公報、特公昭５８－２２３２号公報、特公昭６１－２６４１９号公報、特開平７－４７２７２号公報、特開平１０－４３５９５号公報、特開平４－１１８０５１号公報等に、モリブデン、ビスマス、鉄に加えその他成分の添加による改良、鉄、アンチモンに加えその他成分の添加による改良が開示されている。

さらに、調製法の改良によっても目的生成物収率向上の努力が続けられてきた。例えば、特開平６－９５３０号公報の実施例には９０℃で３時間加熱する方法が、特許２６４０３５６号公報、特開平１－２６５０６８号公報には、スラリーをｐＨ５以下に調整し、５０～１２０℃で加熱処理する方法が、特許２７４７９２０号公報、特開平２－２５１２５０号公報、特開２０００－５６０３号公報、特開２０００－３４４７２４号公報、特開２０００－３７６３１号公報、特開２０００－４２４１４号公報には、スラリーをｐＨ６以上に調整し、５０～１２０℃で加熱処理する方法などが開示されている。

オレフィンの酸化反応、アンモ酸化反応のようなコモディティケミカルにおいては、特公昭５８－８８９５号公報に示されているように所望の生成物の収率を

１％上昇させることにより驚くべき経済効果をあげることができることから、前記のように触媒改良の研究努力が絶えず行われている。

従来技術による触媒は目的のアンモ酸化生成物の収率を徐々に改善してきたものの、未だ必ずしも充分満足できる収率を与えるものではない。また、再現性良く高活性且つ高収率の触媒を製造することも重要な課題の一つとして残されている。

発明の開示

本発明者らは、前記の課題を解決するために鋭意検討した結果、特定の金属元素の原料を含むスラリーを特定の条件下で濃縮処理することにより高活性で、且つ目的とするアンモ酸化生成物を高収率で与える触媒が再現性よく製造できることを見出して本発明に到達した。

すなわち、本発明は、（１）モリブデン、（２）ビスマス、（３）鉄、（４）ニッケル、（５）リチウム、ナトリウム、カリウム、ルビジウム、セシウム及びタリウムからなる群より選ばれた少なくとも一種の元素並びに（６）シリカを必須成分として含む複合酸化物触媒を製造する方法において、前記必須成分のうち少なくとも（１）、（２）、（３）及び（６）を含むスラリーを温度５０～１２０℃の範囲で、濃縮処理前後のスラリー濃度差が２～１５質量％になるように濃縮処理することを特徴とするモリブデン－ビスマス－鉄含有複合酸化物流動層触媒の製法に関する。

発明を実施するための最良の形態

以下、本発明をより具体的に説明する。

本発明で用いる流動層触媒を製造するに際しては、触媒成分として（１）モリブデン、（２）ビスマス、（３）鉄、（４）ニッケル、（５）リチウム、ナトリウム、カリウム、ルビジウム、セシウム及びタリウムからなる群より選ばれた少なくとも一種の元素並びに（６）シリカを必須成分として含む複合酸化物触媒を製造する方法において、前記必須成分のうち少なくとも（１）、（２）、（３）及び（６）を含むスラリーを温度５０～１２０℃の範囲で、濃縮処理前後のスラ

リー濃度差が２～１５質量％になるように濃縮処理することが要件であり、これらの構成要件のうちいずれの要件が欠けても本発明の目的を達成することはできない。

ここでいう濃縮処理とはスラリー中の水分を蒸発させ処理後のスラリー濃度を高める工程のことである。濃縮処理時の水分の蒸発速度は制御されていることが好ましく、そのため還流器を用いたり、水を添加して蒸発水分量を調整しながら行っても良い。

濃縮処理を行うスラリー中には少なくとも前記成分（１）、（２）、（３）及び（６）の原料が含まれている必要がある。これらを同時に含むスラリーを濃縮処理することで高いアンモ酸化反応収率を与える触媒を再現性良く得ることができる。濃縮処理に際しては必ずしもこれらの各成分原料の全量を含む必要はなく、一部分を濃縮処理後のスラリーに添加しても差し支えない。

濃縮処理によってアンモ酸化生成物の収率が向上する理由は未だ明らかではないが、濃縮処理により触媒活性向上等に好ましい化合物あるいは前駆体構造の生成、スラリー中の沈殿の微細化等が促進されたためと考えられる。同時にスラリーが安定化され、高性能な触媒を再現性良く得られるものと考えられる。

濃縮処理時のスラリー温度は、５０～１２０℃の範囲が好ましく、より好ましくは９０～１２０℃の範囲である。これ未満の温度では十分な効果が得られない場合があり、これを超える温度では効果はあるものの濃縮系を加圧にする必要があり、経済的に非合理的である。濃縮時の圧力は減圧、常圧、加圧のいずれも可能であるが、減圧系及び常圧系が好ましく、特に常圧系が経済的に合理的である。

濃縮処理の時間は特に限定されないが、通常は３０分以上、好ましくは１～１０時間の範囲である。また、２４時間を超える濃縮時間は生産効率の面から好ましくない。

濃縮前後のスラリーの濃度差は、２～１５質量％が好ましく、より好ましくは３～１４質量％である。ここでいうスラリー濃度とは、「スラリー全体の質量」に対する「そのスラリーを構成する成分元素を触媒の最終形態である安定な酸化物に換算した質量」の割合のことで、濃縮前後のスラリーの濃度差が小さ過ぎると十分な効果が得られず、大きすぎるとスラリー粘度の上昇等によりその後の噴

霧乾燥工程に支障をきたす恐れがある。このため、濃縮処理後のスラリー濃度は、１５～３５質量％の範囲が好ましく、より好ましくは１６～３０質量％の範囲である。

濃縮処理を行うスラリーの性状には特に限定はないが、ｐＨが１～４の範囲に調整されたスラリーであることが好ましい。特に、ｐＨがこの範囲にあるスラリー中ではシリカ原料として用いるシリカゾルが準安定領域にあるためそのほとんどが液相部に存在しており、従来技術では実用に耐え得る粒子強度を有する触媒を得るための噴霧乾燥条件等に制約を受ける場合があった。しかしながら、このようなｐＨ範囲のスラリーであっても本発明による濃縮処理を施すことにより、アンモ酸化生成物の収率向上だけでなく、粒子強度も併せて向上させることができる。そのため、噴霧乾燥条件の制約が少なくなり、触媒製造の生産性を向上させることができる。

濃縮処理による触媒の粒子強度向上の理由は未だ明らかではないが、濃縮処理によるシリカの結晶成長あるいは結晶間架橋が促進されたためと考えられる。

ｐＨを比較的低く調整する工程を含む製法をとるときは特許２６４０３５６号公報記載の方法に準じた方法を、ｐＨを比較的高く調整する工程を含む製法をとるときは特許２７４７９２０号公報記載の方法に準じた方法を用いることができる。また、特許２７４７９２０号公報に示されているようにスラリーのゲル化抑制のためキレート剤、例えばエチレンジアミン四酢酸、乳酸、クエン酸、酒石酸、グルコン酸等を共存させる方法を併用することもできる。これらキレート剤は、調整ｐＨが比較的低い、例えば1～３の範囲にする時にも少量加えることにより効果を示すことがある。

本発明による調製法を適用する触媒組成は（１）モリブデン、（２）ビスマス、（３）鉄、（４）ニッケル、（５）リチウム、ナトリウム、カリウム、ルビジウム、セシウム及びタリウムからなる群より選ばれた少なくとも一種の元素並びに（６）シリカを必須成分として含むものであれば特に限定はされないが、下記の一般式で表される組成を有する触媒に適用することが好ましい。

$Mo_{10}\,Bi_a\,Fe_b\,Ni_c\,(Fe\,Sb_d)_e\,F_f\,G_g\,H_h\,M_m\,X_x\,Y_y\,O_i\,(SiO_2)_j$

（式中、Ｍｏ、Ｂｉ、Ｆｅ、Ｎｉ及び（ＦｅＳｂｄ）は、それぞれモリブデン、

ビスマス、鉄、ニッケル及びアンチモン酸鉄を示し、Ｆはイットリウム、ランタン、セリウム、プラセオジム、ネオジム、サマリウム、アルミニウム及びガリウムからなる群から選ばれた少なくとも一種の元素、Ｇはマグネシウム、カルシウム、ストロンチウム、バリウム、クロム、マンガン、コバルト、銅、亜鉛及びカドミウムからなる群から選ばれた少なくとも一種の元素、Ｈはチタン、ジルコニウム、バナジウム、ニオブ、タンタル、タングステン、ゲルマニウム、錫、鉛及びアンチモンからなる群から選ばれた少なくとも一種の元素、Ｍはルテニウム、ロジウム、パラジウム、レニウム、オスミウム、イリジウム、白金及び銀からなる群から選ばれた少なくとも一種の元素、Ｘは硼素、燐及びテルルからなる群から選ばれた少なくとも一種の元素、Ｙはリチウム、ナトリウム、カリウム、ルビジウム、セシウム及びタリウムからなる群から選ばれた少なくとも一種の元素、Ｏは酸素、ＳｉＯ２はシリカを、そして添字ａ、ｂ、ｃ、ｄ、ｅ、ｆ、ｇ、ｈ、ｍ、ｘ、ｙ、ｉ及びｊは原子比を示し、Ｍｏ＝１０の時、ａ＝０．２～１．５、好ましくは０．３～１．２、ｂ＝０．７～１５、好ましくは０．８～１３、ｃ＝３～１２、好ましくは４～１０、ｄ＝０．８～２、好ましくは０．９～１．５、ｅ＝０～２０、ｆ＝０．１～１．５、好ましくは０．２～１．４、ｇ＝０～３、ｈ＝０～５、ｍ＝０～１．０、ｘ＝０～３、ｙ＝０．０５～１．５、好ましくは０．０８～１．２、ｉ＝上記各成分が結合して生成する金属酸化物の酸素の数、ｊ＝２０～２００、好ましくは３０～１５０である。）

本発明の触媒を構成する各元素の出発原料としては特に制限されるものではないが、例えばモリブデン成分の原料としては三酸化モリブデンのようなモリブデン酸化物、モリブデン酸、パラモリブデン酸アンモニウム、メタモリブデン酸アンモニウムのようなモリブデン酸またはその塩、リンモリブデン酸、ケイモリブデン酸のようなモリブデンを含むヘテロポリ酸またはその塩などを用いることができる。

ビスマス成分の原料としては硝酸ビスマス、炭酸ビスマス、硫酸ビスマス、酢酸ビスマスなどのビスマス塩、三酸化ビスマス、金属ビスマスなどを用いることができる。これらビスマス成分の原料は固体のままあるいは水溶液や硝酸溶液、それらの水溶液から生じるビスマス化合物のスラリーとして用いることができる

が、硝酸塩、あるいはその溶液、またはその溶液から生じるスラリーを用いることが好ましい。

鉄成分の原料としては酸化第一鉄、酸化第二鉄、四三酸化鉄、硝酸第一鉄、硝酸第二鉄、硫酸鉄、塩化鉄、鉄有機酸塩、水酸化鉄等を用いることができるほか、金属鉄を加熱した硝酸に溶解して用いてもよい。

ニッケル成分の原料としては硝酸ニッケル、水酸化ニッケル、酸化ニッケルなどを用いることができる。

シリカの原料としては、シリカゾル、ヒュームド・シリカ等が用いられるが、シリカゾルを用いるのが便利である。その他の元素の原料としては通常は酸化物あるいは強熱することにより酸化物になり得る硝酸塩、炭酸塩、有機酸塩、水酸化物等またはそれらの混合物が用いられる。

触媒組成中にアンチモン酸鉄を含有させる場合は、あらかじめアンチモン酸鉄を調製した後にモリブデン等その他成分と混合してスラリーを形成するのが好ましい。アンチモン酸鉄は、特開平４－１１８０５１号公報、特開平１０－２３１１２５号公報等に記載されているＦｅＳｂＯ４なる化学式で示される化合物であり、触媒のＸ線回折により存在を確認することができる。その調製法としては、種々提案されているが、例えば、特開平４－１１８０５１号公報、特開平１０－２３１１２５号公報等に記載の方法から適宜選択して用いればよい。このアンチモン酸鉄は、アンチモンと鉄以外の元素を少量含有していてもよい。アンチモン酸鉄の存在は、アンモ酸化生成物の選択性向上、流動層触媒としての物性向上に寄与する。

本発明の方法により濃縮処理等の工程を経て調整されたスラリーは、噴霧乾燥、焼成することにより目的の流動層触媒とすることができる。

本発明の方法で調製したスラリーの噴霧乾燥で用いる噴霧乾燥装置としては、回転円盤式、ノズル式等一般的なものでよい。噴霧乾燥の条件を調節し、流動層触媒として好ましい粒径の触媒が得られるように行う。乾燥後、２００～５００℃の範囲で焼成したのち、更に５００～７００℃の範囲で０．１～２０時間焼成する。焼成雰囲気は、酸素含有ガスが好ましい。空気中で行うのが便利であるが、酸素と窒素、炭酸ガス、水蒸気等を混合して用いることもできる。焼成には、箱

型炉、トンネル炉、回転焼成炉、流動焼成炉等が用いられるが、この中でも流動焼成炉を用いるのが好ましい。

この様にして製造される流動層触媒の粒径は、５～２００μｍ、好ましくは１０～１５０μｍの範囲とするのが良い。

本発明の触媒は有機化合物のアンモ酸化反応に用いられる。本発明の触媒を用いるアンモ酸化反応に供される有機化合物としてはオレフィン、アルコール、エーテル、芳香族化合物及びヘテロ芳香族化合物などが挙げられ、例えばプロピレン、イソブテン、メタノール、エタノール、ターシャリーブタノール、メチルターシャリーブチルエーテル、トルエン、キシレン、ピコリン、キナルジンなどを例示することができる。特にプロピレン、イソブテン、メタノール及びターシャリーブタノールのアンモ酸化反応に適用することにより、好ましい結果が得られる。

本発明のアンモ酸化反応は、通常、原料有機化合物／アンモニア／空気が１／０．９～３／８～１２（モル比）の組成範囲の供給ガスを用い、反応温度は３７０～５００℃、反応圧力は常圧～５００ｋＰａで行う。見掛け接触時間は０．１～２０ｓｅｃである。酸素源としては空気を用いるのが便利であるが、これを水蒸気、窒素、炭酸ガス、飽和炭化水素等で希釈して用いても良いし、酸素を富化して用いるのも良い。

ただし、触媒構造的に安定な本発明の流動層触媒も、反応を続けているとモリブデン成分の逃散によるアンモ酸化生成物収率の低下が観察される。この種の流動層触媒を用いるアンモ酸化反応の反応温度は４００℃を超えるものであり、反応時のモリブデン成分の逃散は避けがたいものと考えられる。このような流動層触媒の反応使用において、長期間性能を維持する方法としては、特公昭５８－５７４２２号公報、ＤＥ３，３１１，５２１Ｃ２号公報、ＷＯ９７／３３８６３号公報等に開示されているようなモリブデン成分を反応中に添加する方法等が知られている。

本発明においても、高位のアンモ酸化生成物収率を長期間維持する上で、モリブデン成分を添加しつつ反応することが好ましい。ここで用いられるモリブデン成分としては、金属モリブデン、三酸化モリブデン、モリブデン酸、ジモリブデ

ン酸アンモニウム、パラモリブデン酸アンモニウム、オクタモリブデン酸アンモニウム、ドデカモリブデン酸アンモニウム、燐モリブデン酸等があげられる。気体、液体の状態としても使用できるが、これらモリブデン成分を固体の状態として用いるのが実際的である。また、これらモリブデン成分を不活性物質または触媒に担持して用いても良い。特にモリブデン成分を触媒に富化して用いる方法は有効である。この方法は添加したモリブデンの利用効率が良く、系内の酸化モリブデン析出などによるトラブル発生が抑制されるなど好ましい使用形態である。モリブデン富化触媒の製法は、特開平１１－３３４００号公報に記載の方法などを適用することができる。

これらモリブデン成分を連続的にまたは断続的に反応器に加える。添加時期並びに添加量は反応成績の推移により適宜決めればよいが、一時に添加する量は、充填触媒に対して、０．０５～２質量％の範囲とするのが良い。一時に多量に加えても、いたずらに反応系外へ逃散し、無駄に消費されてしまう上、反応器内へ沈着堆積したりして運転上問題を生じたりするので注意が必要である。

以下、本発明を実施例及び比較例により具体的に説明する。

（触媒の活性試験）

触媒の活性試験はプロピレンのアンモ酸化反応を例として次のように行った。その活性試験結果を表－１に示した。

触媒流動部の内径が２５ｍｍ、高さ４００ｍｍの流動層反応器に触媒を充填し、プロピレン／アンモニア／空気／水蒸気　＝　１／１．２／９．５／０．５（モル比）の組成の混合ガスをガス線速度４．５ｃｍ／ｓｅｃで送入した。反応圧力は２００ｋＰａとした。

なお、反応時にモリブデン成分を富化した触媒を、充填触媒に対して、モリブデンとして０．１～０．２質量％を１００ないし５００時間の間隔で加えた。

接触時間（ｓｅｃ）＝　見掛け嵩密度基準の触媒容積（ｍｌ）／反応条件に換算した供給ガス流量（ｍｌ／ｓｅｃ）

アクリロニトリル収率（％）＝　生成したアクリロニトリルのモル数／供給したプロピレンのモル数×１００

（触媒の強度試験）

実施例及び比較例において製造した触媒の粒子強度は、特開平９－７０５４２号公報記載の方法に準じ、以下の方法により測定し、圧縮強度［Ｎ（ニュートン）／粒］として表－２に示した。

装置：島津製作所製「島津ＭＣＴＭ－２００」

圧子：上部加圧圧子　　ダイヤモンド製　　５００μｍ平面圧子

下部加圧版：ＳＵＳ製

負荷速度：７．０６×１０$^{-3}$Ｎ／ｓｅｃ

サンプル：４５～５０μｍ粒子の触媒

なお、４５～５０μｍの供与粒子はＢｕｃｋｅｅ　Ｍｅａｒｓ．Ｃｏ．Ｓｔ．Ｐａｕｌ製マイクロ・メッシュ・プレシジョン・シーブスを用いて篩別することによって得たものである。この４５～５０μｍ粒子から無作為に選んだ３０粒の測定値の平均をもって、サンプルの圧縮強度［Ｎ／粒］とした。

実施例 1

組成が、$Mo_{10}\ Bi_{0.4}\ Fe_{1.2}\ Ni_{6.0}\ Ce_{0.3}\ Cr_{0.8}\ P_{0.1}\ B_{0.1}\ K_{0.2}\ O_i\ (SiO_2)_{35}$（i は他の元素の原子価により自然に決まる値であるので以下酸素の記載を省略する）である流動層触媒を以下の要領で製造した。

純水３００ｇにパラモリブデン酸アンモニウム４０９．４ｇを溶解し、ついで８５％燐酸２．７ｇ及び無水硼酸０．５ｇをそれぞれ加える。この液へ３．３％硝酸２７０ｇに硝酸ビスマス４５．０ｇ、硝酸カリウム４．７ｇ、硝酸ニッケル４０４．７ｇ、硝酸クロム７４．２ｇ、硝酸セリウム３０．２ｇ、クエン酸２５．０ｇを溶解した液を混合した。ついで２０％シリカゾル２４３８．６ｇを加えた。純水２７０ｇに硝酸鉄１１２．４ｇとクエン酸２５．０ｇを溶解した液を調製し、これに加えた。このスラリーを撹拌しつつ１５％アンモニア水を加え、ｐＨを２．２に調整した。この時のスラリー濃度は２１．１質量％であった。これをスラリー濃度が２８．８質量％となるように１０２℃で７時間濃縮処理した。

この様にして調製したスラリーを回転円盤式噴霧乾燥機で、入口温度を３３

０℃、出口温度を１６０℃として噴霧乾燥した。この乾燥粒子を２５０℃で２時間、４００℃で２時間熱処理し、最終的に６５０℃で３時間流動焼成した。

実施例２

組成が、Mo10 Bi0.5 Fe1.1 Ni4.0 Ce0.4 La0.2 Cr1.0 Co2.0 P0.2 B0.2 K0.2 Si35 である流動層触媒を実施例 1 と同様の方法により製造し、表－１の条件で焼成した。但し、Ｌａ、Ｃｏ原料は硝酸塩を使用し、硝酸ニッケルの次に加えた。

実施例３

組成が、Mo10 Bi0.5 Fe1.3 Ni5.0 Ce0.3 Cr0.6 Mg1.0 Zr0.2 K0.2 Si35 である流動層触媒を実施例 1 と同様の方法により製造し、表－１の条件で焼成した。但し、Ｍｇ、Ｚｒ原料は硝酸塩を使用し、硝酸ニッケルの次に加えた。

実施例４

組成が、Mo10 Bi0.3 Fe1.1 Ni6.0 Ce0.2 Pr0.1 Cr0.8 Zn0.2 P0.3 K0.1 Rb0.1 Si40 である流動層触媒を実施例 1 と同様の方法により製造し、表－１の条件で焼成した。但し、Ｐｒ、Ｚｎ、Ｒｂ原料は硝酸塩使用し、硝酸ニッケルの次に加えた。

実施例５

組成が、Mo10 Bi0.4 Fe0.9 Ni5.5 Ce0.4 Cr1.2 Mn0.4 W0.4 Pd0.01 P0.2 B0.2 K0.2 Si35 である流動層触媒を実施例 1 と同様の方法により製造し、表－１の条件で焼成した。但し、Ｍｎ、Ｐｄ原料は硝酸塩を使用し、硝酸ニッケルの次に加え、Ｗ原料はパラタングステン酸アンモニウムを使用し、パラモリブデン酸アンモニウムの次に加えた。

実施例６

組成が、Mo10 Bi0.4 Fe1.2 Ni6.0 (Fe Sb1.1)3 Ce0.3 Cr0.8 P0.1 B0.1 K0.2 Si35 である流動層触媒を以下の要領で製造した。

純水３００ｇにパラモリブデン酸アンモニウム３４８．９ｇを溶解し、ついで

８５％燐酸２．３ｇ及び無水硼酸０．４ｇをそれぞれ加える。この液へ３．３％硝酸２７０ｇに硝酸ビスマス３８．４ｇ、硝酸カリウム４．０ｇ、硝酸ニッケル３４４．９ｇ、硝酸クロム６３．３ｇ、硝酸セリウム２５．７ｇ、クエン酸２５．０ｇを溶解した液を混合した。ついで２０％シリカゾル２０７８．６ｇを加えた。純水２７０ｇに硝酸鉄９５．８ｇとクエン酸２５．０ｇを溶解した液を調製し、これに加えた。このスラリーを撹拌しつつ１５％アンモニア水を加え、ｐＨを２．３に調整した。この時のスラリー濃度は２１．１質量％であった。これをスラリー濃度が２８．８質量％となるように１０２℃で７時間濃縮処理した。ついで４０％アンチモン酸鉄スラリー３６９．１ｇを加えた。

この様にして調製したスラリーを回転円盤式噴霧乾燥機で、入口温度を３３０℃、出口温度を１６０℃として噴霧乾燥した。この乾燥粒子を２５０℃で２時間、４００℃で２時間熱処理し、最終的に６５０℃で３時間流動焼成した。

実施例７

組成が実施例３と同じである流動層触媒を以下の要領で製造した。

純水２０００ｇにパラモリブデン酸アンモニウム４０９．８ｇを溶解し、この液へ３．３％硝酸２７０ｇに硝酸ビスマス５６．３ｇ、硝酸カリウム４．７ｇ、硝酸ニッケル３３７．６ｇ、硝酸クロム５５．７ｇ、硝酸セリウム３０．２ｇ、硝酸マグネシウム５９．５ｇ、硝酸ジルコニウム１２．４ｇ、クエン酸２５．０ｇを溶解した液を混合した。ついで２０％シリカゾル２４４１．０ｇを加えた。純水２７０ｇに硝酸鉄１２１．９ｇとクエン酸２５．０ｇを溶解した液を調製し、これに加えた。このスラリーを撹拌しつつ１５％アンモニア水を加え、ｐＨを２に調整した。この時のスラリー濃度は１４．７質量％であった。これをスラリー濃度が２１．１質量％となるように１０２℃で２時間濃縮処理した。

この様にして調製したスラリーを回転円盤式噴霧乾燥機で、入口温度を３３０℃、出口温度を１６０℃として噴霧乾燥した。この乾燥粒子を２５０℃で２時間、４００℃で２時間熱処理し、最終的に６５０℃で３時間流動焼成した。

実施例８

組成が実施例１と同じである流動層触媒を以下の要領で製造した。

純水３０００ｇにパラモリブデン酸アンモニウム４０９．４ｇを溶解し、ついで８５％燐酸２．７ｇ及び無水硼酸０．５ｇをそれぞれ加える。この液へ３．３％硝酸２７０ｇに硝酸ビスマス４５．０ｇ、硝酸カリウム４．７ｇ、硝酸ニッケル４０４．７ｇ、硝酸クロム７４．２ｇ、硝酸セリウム３０．２ｇ、クエン酸２５．０ｇを溶解した液を混合した。ついで２０％シリカゾル２４３８．６ｇを加えた。このスラリーを撹拌しつつ１５％アンモニア水を加え、ｐＨを５．０に調整した。これを９９℃で１．５時間加熱処理した。純水２７０ｇに硝酸鉄１１２．４ｇとクエン酸２５．０ｇを溶解して調製した液をこれに加えた。この時のスラリー濃度は１３．０質量％で、ｐＨは４．８であった。これをスラリー濃度が２２．４質量%となるように１０２℃で４時間濃縮処理した。

この様にして調製したスラリーを回転円盤式噴霧乾燥機で、入口温度を３３０℃、出口温度を１６０℃として噴霧乾燥した。この乾燥粒子を２５０℃で２時間、４００℃で２時間熱処理し、最終的に６４０℃で３時間流動焼成した。

実施例９

組成が、Mo10 Bi0.6 Fe0.7 Ni7.0 (Fe Sb1.1)4.5 Ce0.5 P0.2 B0.2 Te0.25 K0.6 Si40 である流動層触媒を以下の要領で製造した。

純水１２００ｇにパラモリブデン酸アンモニウム１８０．６ｇを溶解し、次いで８５％燐酸３．９ｇ、２０％シリカゾル２０４９．１ｇを順次加えた。この液へ３．３％硝酸２７０ｇに硝酸ニッケル３４７．１ｇ、硝酸セリウム３７．０ｇ、硝酸カリウム１０．３ｇ、クエン酸２５ｇ、硝酸ビスマス４９．６ｇを溶解した液を混合した。このスラリーを撹拌しつつ１５％アンモニア水を加え、ｐＨ７．７とし、次いで還流下９９℃で１．５時間加熱処理した。水２５０ｇに金属テルル５．４ｇ、パラモリブデン酸アンモニウム４．５ｇ、過酸化水素水２０ｇを加え、９５～１００℃で撹拌し、溶解した。この液を常温まで冷却し、クエン酸２５ｇ、硝酸鉄４８．２ｇを溶解した。これを撹拌しつつ１５％アンモニア水を加えｐＨ９．２とし、さらにパラモリブデン酸アンモニウム１１５．９ｇを少しずつ加え溶解した。ここでアンモニア水を加えｐＨ７とした。この液を先に加熱処

理したスラリーに混合し、４０％アンチモン酸鉄スラリー４８０．８ｇを混合した。この時のスラリー濃度は１３．８質量％で、ｐＨは７．２であった。これをスラリー濃度が１７．２質量％となるように１０２℃で５．５時間濃縮処理した。

この様にして調製したスラリーを回転円盤式噴霧乾燥機で、入口温度を３３０℃、出口温度を１６０℃として噴霧乾燥した。この乾燥粒子を２５０℃で２時間、４００℃で２時間熱処理し、最終的に５８０℃で３時間流動焼成した。

実施例１０

組成が実施例１と同じである流動層触媒を以下の要領で製造した。

純水３０００ｇにパラモリブデン酸アンモニウム４０９．４ｇを溶解し、ついで８５％燐酸２．７ｇ及び無水硼酸０．５ｇをそれぞれ加える。この液へ３．３％硝酸２７０ｇに硝酸ビスマス４５．０ｇ、硝酸カリウム４．７ｇ、硝酸ニッケル４０４．７ｇ、硝酸クロム７４．２ｇ、硝酸セリウム３０．２ｇ、クエン酸２５．０ｇを溶解した液を混合した。ついで２０％シリカゾル２４３８．６ｇを加えた。純水２７０ｇに硝酸鉄１１２．４ｇとクエン酸２５．０ｇを溶解した液を調製し、これに加えた。このスラリーを撹拌しつつ１５％アンモニア水を加え、ｐＨを３．０に調整した。これを９９℃で１．５時間加熱処理した。この時のスラリー濃度は１２．５質量％であった。これをスラリー濃度が２２．１質量％となるように１０２℃で４時間濃縮処理した。

この様にして調製したスラリーを回転円盤式噴霧乾燥機で、入口温度を３３０℃、出口温度を１６０℃として噴霧乾燥した。この乾燥粒子を２５０℃で２時間、４００℃で２時間熱処理し、最終的に６５０℃で３時間流動焼成した。

比較例１

濃縮処理７時間を行わなかった以外は実施例１と同様の方法で、実施例１と同一組成の流動層触媒を製造し、表－１の条件で焼成した。

比較例２

濃縮処理するところを９９℃で２時間加熱処理に変更したこと以外は実施例７

と同様の方法で、実施例３と同一組成の流動層触媒を製造し、表－１の条件で焼成した。

比較例３

濃縮処理７時間を行わなかった以外は実施例６と同様の方法で、実施例６と同一組成の流動層触媒を製造し、表－１の条件で焼成した。

比較例４

硝酸鉄とクエン酸の溶液を濃縮処理の次に加えたこと以外は実施例８と同様の方法で、実施例１と同一組成の流動層触媒を製造し、表－１の条件で焼成した。

これら実施例並びに比較例の触媒を用い、上記の反応条件下、プロピレンのアンモ酸化反応をおこなった。

結果を下表に示した。

表1－1

		Mo	Bi	Fe	Ni	FeSb Fe Sb	F	G	H	M	X	Y	SiO_2
実施例	1	10	0.4	1.2	6.0		Ce 0.3	Cr 0.8			P B 0.1 0.1	K 0.2	35
	2	10	0.5	1.1	4.0		Ce La 0.4 0.2	Cr Co 1.0 2.0			P B 0.2 0.2	K 0.2	35
	3	10	0.5	1.3	5.0		Ce 0.3	Cr Mg 0.6 1.0	Zr 0.2			K 0.2	35
	4	10	0.3	1.1	6.0		Ce Pr 0.2 0.1	Cr Zn 0.8 0.2			P 0.3	K Rb 0.1 0.1	40
	5	10	0.4	0.9	5.5		Ce 0.4	Cr Mn 1.2 0.4	W 0.4	Pd 0.01	P B 0.2 0.2	K 0.2	35
	6	10	0.4	1.2	6.0	3.0 3.3	Ce 0.3	Cr 0.8			P B 0.1 0.1	K 0.2	35
	7	10	0.5	1.3	5.0		Ce 0.3	Cr Mg 0.6 1.0	Zr 0.2			K 0.2	35
	8	10	0.4	1.2	6.0		Ce 0.3	Cr 0.8			P B 0.1 0.1	K 0.2	35
	9	10	0.6	0.7	7.0	4.5 5	Ce 0.5				P B Te 0.2 0.2 0.25	K 0.6	40
	1 0	10	0.4	1.2	6.0		Ce 0.3	Cr 0.8			P B 0.1 0.1	K 0.2	35

表1－2

		Mo	Bi	Fe	Ni	FeSb Fe	FeSb Sb	F	G	H	M	X	Y	SiO_2
比較例	1	10	0.4	1.2	6.0			Ce 0.3	Cr 0.8			P 0.1 B 0.1	K 0.2	35
	2	10	0.5	1.3	5.0			Ce 0.3	Cr 0.6 Mg 1.0	Zr 0.2			K 0.2	35
	3	10	0.4	1.2	6.0	3.0	3.3	Ce 0.3	Cr 0.8			P 0.1 B 0.1	K 0.2	35
	4	10	0.4	1.2	6.0			Ce 0.3	Cr 0.8			P 0.1 B 0.1	K 0.2	35

表1－3

		濃縮処理				焼成温度 [℃]	接触時間 [sec]	アクリロニトリル収率[%] 経過時間[h]			圧縮強度 ×10^{-3} [N/粒]
		濃縮前 pH	濃縮前 濃度 [%]	濃縮後 濃度 [%]	濃縮 時間 [h]			50	500	1000	
実施例	1	2.2	21.1	28.8	7.0	650	2.4	82.9	82.9	83.0	150
	2	2.5	21.1	28.7	7.0	650	2.3	82.6	82.6	82.5	150
	3	2.3	21.0	28.6	7.0	640	2.4	82.8	82.6	82.7	135
	4	1.8	21.1	28.7	7.0	660	2.1	82.5	82.6	82.5	140
	5	2.0	21.0	28.7	7.0	650	2.3	82.6	82.4	82.3	145
	6	2.3	21.1	28.7	7.0	650	2.2	83.1	83.0	83.1	160
	7	2.0	14.7	21.1	2.0	640	2.7	82.5	82.3	82.3	120
	8	2.3	12.6	22.0	4.0	640	2.3	82.8	82.6	82.6	155
	9	7.2	13.8	17.2	5.5	580	2.3	83.1	82.9	82.7	195
	10	3.0	12.5	22.1	4.0	650	2.4	82.7	82.6	82.6	145

表1－4

		濃縮処理				焼成温度 [℃]	接触時間 [sec]	アクリロニトリル収率[%]			圧縮強度 $\times 10^{-3}$ [N/粒]
		濃縮前 pH	濃縮前 濃度 [%]	濃縮後 濃度 [%]	濃縮 時間 [h]			経過時間[h]			
								50	500	1000	
比較例	1	—	濃縮なし 21.1	 21.1	0.0	630	3.3	81.6	81.4	81.1	80
	2	—	濃縮なし 14.7	 14.7	加熱 2.0	640	3.1	81.5	81.5	81.3	100
	3	—	濃縮なし 21.1	 21.1	0.0	630	2.5	82.0	81.7	81.6	85
	4	4.8	13.0	22.4	4.0	640	2.4	81.8	81.7	81.8	90

産業上の可能性

本発明の方法によりモリブデンービスマスー鉄含有複合酸化物流動層触媒を再現性良く製造することができ、更に製造されるモリブデンービスマスー鉄含有複合酸化物流動層触媒は、高活性で、かつ目的とするアンモ酸化生成物を高収率で与え、例えばプロピレンのアンモ酸化反応により収率良くアクリロニトリルを得ることができる。

請求の範囲

1．　（1）モリブデン、（2）ビスマス、（3）鉄、（4）ニッケル、（5）リチウム、ナトリウム、カリウム、ルビジウム、セシウム及びタリウムからなる群より選ばれた少なくとも一種の元素並びに（6）シリカを必須成分として含む複合酸化物触媒を製造する方法において、前記必須成分のうち少なくとも（1）、（2）、（3）及び（6）を含むスラリーを温度５０～１２０℃の範囲で、濃縮処理前後のスラリー濃度差が２～１５質量%になるように濃縮処理することを特徴とするモリブデン－ビスマス－鉄含有複合酸化物流動層触媒の製法。

2．濃縮処理後のスラリー濃度が１５～３５質量%の範囲であることを特徴とする請求項１記載のモリブンデン－ビスマス－鉄含有複合酸化物流動層触媒の製法。

3．濃縮処理前のスラリーのｐＨを１～４の範囲に調整することを特徴とする請求項１又は２に記載のモリブデン－ビスマス－鉄含有複合酸化物流動層触媒の製法。

4．複合酸化物流動層触媒が、下記の一般式で示される組成を有することを特徴とする請求項１～３のいずれか一項に記載のモリブデン－ビスマス－鉄含有複合酸化物流動層触媒の製法。

Mo10 Bia Feb Nic (Fe Sbd)e Ff Gg Hh Mm Xx Yy Oi (SiO2)j

（式中、Ｍｏ、Ｂｉ、Ｆｅ、Ｎｉ及び（ＦｅＳｂｄ）は、それぞれモリブデン、ビスマス、鉄、ニッケル及びアンチモン酸鉄を示し、Ｆはイットリウム、ランタン、セリウム、プラセオジム、ネオジム、サマリウム、アルミニウム及びガリウムからなる群から選ばれた少なくとも一種の元素、Ｇはマグネシウム、カルシウム、ストロンチウム、バリウム、クロム、マンガン、コバルト、銅、亜鉛及びカドミウムからなる群から選ばれた少なくとも一種の元素、Ｈはチタン、ジルコニウム、バナジウム、ニオブ、タンタル、タングステン、ゲルマニウム、錫、鉛及びアンチモンからなる群から選ばれた少なくとも一種の元素、Ｍはルテニウム、

ロジウム、パラジウム、レニウム、オスミウム、イリジウム、白金及び銀からなる群から選ばれた少なくとも一種の元素、Xは硼素、燐及びテルルからなる群から選ばれた少なくとも一種の元素、Yはリチウム、ナトリウム、カリウム、ルビジウム、セシウム及びタリウムからなる群から選ばれた少なくとも一種の元素、Oは酸素、ＳｉＯ２はシリカを、そして添字ａ、ｂ、ｃ、ｄ、ｅ、ｆ、ｇ、ｈ、ｍ、ｘ、ｙ、ｉ及びｊは原子比を示し、Ｍｏ＝１０の時、ａ＝０．２～１．５、ｂ＝０．７～１５、ｃ＝３～１２、ｄ＝０．８～２、ｅ＝０～２０、ｆ＝０．１～１．５、ｇ＝０～５、ｈ＝０～３、ｍ＝０～１．０、ｘ＝０～３、ｙ＝０．０５～１．５、ｉ＝上記各成分が結合して生成する金属酸化物の酸素の数、ｊ＝２０～２００である。）

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP02/03446

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^7 B01J23/88, C07C253/26, 255/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl^7 B01J21/00-37/36

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926-1996	Toroku Jitsuyo Shinan Koho	1994-2002
Kokai Jitsuyo Shinan Koho	1971-2002	Jitsuyo Shinan Toroku Koho	1996-2002

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E,X	JP 2001-187772 A (Mitsubishi Rayon Co., Ltd.), 10 July, 2001 (10.07.01), Claim 1; example 1 (Family: none)	1-4
X A	JP 63-250357 A (Nitto Chemical Industry Co., Ltd.), 18 October, 1988 (18.10.88), Claims; page 4, lower left column, lines 3 to 8; example 1 (Family: none)	1-3 4
X A	EP 340909 A1 (Nitto Chemical Industry Co., Ltd.), 08 November, 1989 (08.11.89), Claims; examples & US 5158787 A & JP 1-257125 A	1-2 3-4

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
02 July, 2002 (02.07.02)	16 July, 2002 (16.07.02)

Name and mailing address of the ISA/	Authorized officer
Japanese Patent Office	
Facsimile No.	Telephone No.

国際調査報告

国際出願番号　ＰＣＴ／ＪＰ０２／０３４４６

Ａ．　発明の属する分野の分類（国際特許分類（ＩＰＣ））
Int. Cl.⁷　B01J23/88, C07C253/26, 255/08

Ｂ．　調査を行った分野
調査を行った最小限資料（国際特許分類（ＩＰＣ））
Int. Cl.⁷　B01J21/00-37/36

最小限資料以外の資料で調査を行った分野に含まれるもの
日本国実用新案公報　1926-1996年
日本国公開実用新案公報　1971-2002年
日本国登録実用新案公報　1994-2002年
日本国実用新案登録公報　1996-2002年

国際調査で使用した電子データベース（データベースの名称、調査に使用した用語）

Ｃ．　関連すると認められる文献

引用文献のカテゴリー＊	引用文献名　及び一部の箇所が関連するときは、その関連する箇所の表示	関連する請求の範囲の番号
EX	JP 2001-187772 A（三菱レイヨン株式会社）2001.07.10，請求項１，実施例１（ファミリーなし）	1-4
X A	JP 63-250357 A（日東化学工業株式会社）1988.10.18，特許請求の範囲、第４頁左下欄第３行～８行、実施例１（ファミリーなし）	1-3 4
X A	EP 340909 A1（日東化学工業株式会社）1989.11.08，特許請求の範囲、実施例 & US 5158787 A & JP 1-257125 A	1-2 3-4

□ Ｃ欄の続きにも文献が列挙されている。　　□ パテントファミリーに関する別紙を参照。

＊　引用文献のカテゴリー
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国際調査を完了した日　０２．０７．０２

国際調査報告の発送日　16.07.02

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特許庁審査官（権限のある職員）　４Ｇ　９３４２
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(54) METHOD FOR PRODUCING MOLYBDENUM-BISMUTH-IRON CONTAINING COMPOSITE OXIDE FLUID BED CATALYST

(57) One object of the present invention is to provide a method for producing a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst, which is useful for an ammoxidation and which produces a target ammoxidation product at high yield and an excellent reproducibility. In order to achieve this object, the present invention provides a method for producing a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst which is used for ammoxidation of organic compounds, comprising the step in that a slurry, which contains the raw materials containing specific elements, is subjected to a concentration treatment at 50-120°C.

EP 1 386 661 A1

Description

TECHNICAL FIELD

[0001] The present invention relates to a method for producing a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst. Specifically, the present invention relates to a method for producing a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst, which is used for an ammoxidation of many kinds of organic compounds.

BACKGROUND ART

[0002] Many catalysts, which are suitably used in methods for producing an ammoxidation product by ammoxidation of olefins, are disclosed in numerous documents. Examined Japanese Patent Application, Second Publication No. Sho 38-17967 discloses an oxide catalyst containing molybdenum, bismuth, and iron. Examined Japanese Patent Application, Second Publication No. Sho 38-19111 discloses an oxide catalyst containing iron and antimony. After these oxide catalysts were improved diligently, many improved oxide catalysts were suggested. For example, Examined Japanese Patent Application, Second Publication No. Sho 51-33888, Unexamined Japanese Patent Application, First Publication No. Sho 55-56839, Examined Japanese Patent Application, Second Publication No. Sho 58-2232, Examined Japanese Patent Application, Second Publication No. Sho 61-26419, Unexamined Japanese Patent Application, First Publication No. Hei 07-47272, Unexamined Japanese Patent Application, First Publication No. Hei 10-43595, Unexamined Japanese Patent Application, First Publication No. Hei 04-118051, and the like disclose solutions for improving an oxide catalyst by adding molybdenum, bismuth, iron, and other components and by adding iron, antimony, and other components.

[0003] In addition, in order to improve a yield of a target product, methods for producing an oxide catalyst have been examined. For example, Unexamined Japanese Patent Application, First Publication No. Hei 06-9530 discloses examples showing a method in which a slurry is heated at 90°C for three hours. Japanese Patent 2,640,356 and Unexamined Japanese Patent Application, First Publication No. Hei 01-265068 disclose a method in which a pH of a slurry is adjusted to 5 or less and it is heated to 50-120°C. Japanese Patent 2,747,920, Unexamined Japanese Patent Application, First Publication No. Hei 02-251250, Unexamined Japanese Patent Application, First Publication No. 2000-5603, Unexamined Japanese Patent Application, First Publication No. 2000-344724, Unexamined Japanese Patent Application, First Publication No. 2000-37631, and Unexamined Japanese Patent Application, First Publication No. 2000-42414 disclose a method in which a pH of a slurry is adjusted to 6 or more and it is heated to 50-120°C.

[0004] As disclosed in Examined Japanese Patent Application, Second Publication No. Sho 58-8895, in chemical products, which are produced by an oxidation or an ammoxidation of olefins, marvelous economical effects can be obtained by increasing only 1% of a yield thereof. Due to this, research to improve the catalysts is constantly being performed.

[0005] Conventional catalysts gradually improve a yield of target ammoxidation products. However, conventional catalysts do not achieve sufficient yield. In addition, it has been an objective to produce a catalyst having a high activity at high yield and an excellent reproducibility, as one of serious problems to be solved.

DISCLOSURE OF INVENTION

[0006] As a result of conducting diligent research, the present inventors have demonstrated that a catalyst which yields an objective ammoxidation product, having a high activity at high yield and an excellent reproducibility, can be produced by concentrating a slurry containing specified metal elements under specified conditions.

[0007] In other words, the present invention relates to a method for producing a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst which is a method for producing a composite oxide catalyst containing components (1) molybdenum, (2) bismuth, (3) iron, (4) nickel, (5) at least one element selected from lithium, sodium, potassium, rubidium, cesium and thallium, and (6) silica, as essential components, wherein a slurry containing at least components (1), (2), (3), and (6) is subjected to a concentration treatment in a range of 50-120°C, so that the concentration difference of the slurry between before and after the concentration treatment is in a range of 2-15% by mass.

MODES FOR CARRYING OUT THE INVENTION

[0008] The present invention is explained in detailed below.

[0009] In order to produce the fluid bed catalyst in the present invention, in a method for producing a composite oxide catalyst containing components (1) molybdenum, (2) bismuth, (3) iron, (4) nickel, (5) at least one element selected from lithium, sodium, potassium, rubidium, cesium and thallium, and (6) silica, as essential components, a slurry con-

taining at least components (1), (2), (3), and (6) is subjected to a concentration treatment in a range of 50-120°C, so that the concentration difference of the slurry between before and after the concentration treatment is in a range of 2-15% by mass. If one of these requirements is not satisfied, the objects of the present invention cannot be achieved.

[0010] The concentration treatment denotes a step in which a slurry concentration after a concentration treatment is increased by evaporating moisture contained in the slurry. In the concentration treatment, an evaporation rate of moisture is preferably adjusted. In order to adjust the evaporation rate, a reflux apparatus may be used. In addition, the concentration treatment may be also carried out while the evaporation amount of moisture is adjusted by adding water.

[0011] The slurry, which is subjected to the concentration treatment, must contain at least components (1), (2), (3), and (6). The catalyst, which produces a high ammoxidation product yield, is produced with an excellent reproducibility by concentrating the slurry containing components (1), (2), (3), and (6). Moreover, it is not necessary for the slurry to contain the required total amount of these components in the concentration treatment; a part of amount of the component may be added to the slurry after the concentration treatment.

[0012] The reasons for improving the yield of the ammoxidation products by the concentration treatment are not clear. However, it is believed that by the concentration treatment, a compound or a precursor which is suitable for improving the catalyst activity is formed. Otherwise, it is also believed that precipitates in the slurry become finer in good progress and the slurry is stabilized. Due to this, it is believed that a catalyst having superior properties is produced with a good reproducibility.

[0013] A slurry temperature in the concentration treatment is preferably in a range of 50-120°C, and more preferably in a range of 90-120°C. When the slurry temperature is less than 50°C, there are cases in which sufficient effects cannot be obtained. When it exceeds 120°C, the effects can be obtained, but the system used for the concentration treatment must be pressurized, and this is not economical. During the concentration treatment, the pressure may be reduced, normal, or increased. However, the concentration treatment is preferably carried out under reduced pressure or normal pressure. In particular, normal pressure is more preferable economically.

[0014] The duration of the concentration treatment is not restricted, in particular. In general, the concentration treatment is carried out for 30 minutes or longer, and more preferably it is carried out for 1-10 hours. The concentration treatment, of which the duration exceeds 24 hours, is not preferably in production efficiency.

[0015] The concentration difference of the slurry between before and after the concentration treatment is preferably in a range of 2-15% by mass, and more preferably in a range of 3-14% by mass. The slurry concentration denotes the ratio of mass of stabilized oxides, which are final products when the component elements contained in the slurry are changed into stabilized oxides, with respect to the total mass of the slurry. When the concentration difference of the slurry before and after the concentration treatment is less than 2% by mass, sufficient effects cannot be obtained. In contrast, when it exceeds 15% by mass, the viscosity of the slurry increases and there is a possibility that a problem may be generated in a spray-drying step after the concentration treatment. Due to this, the slurry concentration after the concentration treatment is preferably in a range of 15-35% by mass. and more preferably in a range of 16-30% by mass.

[0016] Conditions of the slurry, which is subjected to the concentration treatment, is not restricted. However, the slurry, of which the pH is adjusted in a range of 1-4, is preferable. In the slurry having pH of 1-4, silica sol, which is used as a raw material of silica, is in a metastable state. Almost all of silica sol is in a liquid phase. In conventional methods for producing the catalyst, there are cases in which conditions of a spray-drying step which is necessary to produce a catalyst having sufficient particle strength to practical use, are restricted. However, according to the present invention, when the slurry having a pH of 1-4 is used, by conducting the concentration treatment, not only the yield of ammoxidation products is improved, but also the particle strength is improved. Therefore, in the present invention, the restriction to conditions of a spray-drying step decreases, and productivity of catalyst is improved.

[0017] The reasons for improving the particle strength by the concentration treatment are not clear. However, it is believed that by the concentration treatment, a crystal growth of silica or a cross-linking formation in silica is expedited.

[0018] When a pH of the slurry is relatively low, a method disclosed in Japanese Patent 2,640,356 can be adopted. In contrast, when a pH of the slurry is relatively high, a method disclosed in Japanese Patent 2,747,920 can be adopted. In addition, in order to prevent the slurry from gelling, a chelating agent, such as ethylene diamine tetra-acetic acid, lactic acid, citric acid, tartaric acid, gluconic acid, and the like, can be added in the slurry as disclosed in Japanese Patent 2,747,920. When a small amount of the chelating agent is added to the slurry having a relatively low pH, such as 1-3, the effects for preventing the gellation of slurry are sometimes obtained.

[0019] The composition of the catalyst, which is produced by the present invention, is not restricted, as long as it contains components (1) molybdenum, (2) bismuth, (3) iron, (4) nickel, (5) at least one element selected from lithium, sodium, potassium, rubidium, cesium and thallium, and (6) silica, as essential components. However, the method of the present invention is preferably used to produce the catalyst represented by the following formula.

$$Mo10\ Bia\ Feb\ Nic\ (FeSbd)e\ Ff\ Gg\ Hh\ Mm\ Xx\ Yy\ Oi(SiO_2)j$$

[0020] In the formula, Mo, Bi, Fe, Ni, and (FeSbd) denote molybdenum, bismuth, iron, nickel, and iron antimonate. F denotes at least one element selected from yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, aluminum, and gallium. G denotes at least one element selected from magnesium, calcium, strontium, barium, chromium, manganese, cobalt, copper, zinc, and cadmium. H denotes at least one element selected from titanium, zirconium, vanadium, niobium, tantalum, tungsten, germanium, tin, lead, and antimony. M denotes at least one element selected from ruthenium, rhodium, palladium, rhenium, osmium, iridium, platinum, and silver. X denotes at least one element selected from boron, phosphorus, and tellurium. Y denotes at least one element selected from lithium, sodium, potassium, rubidium, cesium, and thallium. O denotes oxygen. SiO_2 denotes silica. Symbols a, b, c, d, e, f, g, h, m, x, y, i, and j denote atomic ratio. When the atonic ratio of Mo is 10, a is in a range of 0.2-1.5. and preferably in a range of 0.3-1.2; b is in a range of 0.7-15, and preferably in a range of 0.8-13; c is in a range of 3-12, and preferably in a range of 4-10; d is in a range of 0.8-2, and preferably in a range of 0.9-1.5; e is in a range of 0-20; f is in a range of 0.1-1.5, and preferably in a range of 0.2-1.4; g is in a range of 0-3; h is in a range of 0-5; m is in a range of 0-1.0; x is in a range of 0-3; y is in a range of 0.05-1.5, and preferably in a range of 0.08-1.2; i is a number of oxygen element in metal oxides, which are formed by combining these elements; and j is in a range of 20-200, and preferably in a range of 30-150.

[0021] Raw materials of these elements contained in the catalyst are not restricted. For example, the raw material of the molybdenum component contains molybdenum oxides such as molybdenum trioxide; molybdic acid and molybdic acid salt such as ammonium paramolybdate, and ammonium methmolybdate; heteropoly acid containing molybdenum, such as phosphomolybdic acid, and silicomolybdic acid and heteropoly acid salt thereof.

[0022] The raw material of the bismuth component includes, for example, salts of bismuth, such as bismuth nitrate, bismuth carbonate, bismuth sulfate, bismuth acetate; bismuth trioxide; metal bismuth, and the like. These raw materials of bismuth component can be used as a solid as it is, an aqueous solution, a nitrate solution, or a slurry containing a bismuth compound, which is produced from the aqueous solution or the nitrate solution. However, bismuth nitrates, a solution containing bismuth nitrates, and a slurry produced from the solution are preferably used as the raw material of the bismuth component.

[0023] The raw material of the iron component includes, for example, ferrous oxide, ferric oxide, triiron tetroxide, ferrous nitrate, ferric nitrate, iron sulfate, iron chloride, organic acid salt of iron, iron hydroxide, and the like, in addition to a solution which is produced by solving metal iron in hot nitric acid.

[0024] The raw material of the nickel component includes, for example, nickel nitrate, nickel hydroxide, nickel oxide, and the like.

[0025] The raw material of the silica component includes, for example, silica sol, humid silica, and the like. However, silica sol is conveniently used. In general, the raw material of the other elements includes, oxides, and nitrates, carbonates, organic acid salts, hydroxides, and mixture thereof, which are changed into oxides by calcination.

[0026] When iron antimonate is contained in the catalyst, it is preferable to prepare iron antimonate and to mix with molybdenum and other components, and thereby a slurry is produced. Iron antimonate is represented by chemical formula $FeSbO_4$, as disclosed in Unexamined Japanese Patent Application, First Publication Nos. Hei 04-118051 and Hei 10-231125. The presence of iron antimonate can be confirmed by an X-ray diffraction analysis. Many methods for producing the iron antimonate have been suggested. For example, the method may be selected from the methods disclosed in Unexamined Japanese Patent Application, First Publication Nos. Hei 04-118051 and Hei 10-231125. Iron antimonate may contain a small amount of elements other than antimony and iron. The presence of the iron antimonate improves the selectivity of ammoxidation products and properties of the fluid bed catalyst.

[0027] The slurry produced by the concentration treatment in the present invention is changed to the objective fluid bed catalyst by spray drying and calcining.

[0028] A spray dryer used for spray drying the slurry produced by these processes includes, for example, ordinal rotary-disc type spray dryers, and ordinal nozzle type spray dryers, and the like. The catalyst having an objective particle diameter, which is suitable for a fluid bed catalyst, is produced by adjusting the conditions of the spray drying. After drying, the dried product is calcined at 200-500°C, and this is further calcined at 500-700°C for 0.1-20 hours. The calcining is preferably carried out in an oxygen containing gas atmosphere. The calcining is conveniently carried out in air, but this may be carried out in a mixed gas containing oxygen, nitrogen, carbon dioxide gas, water vapor, and the like. Box furnaces, tunnel calciners, rotation calciners, fluidized bed calciners, and the like may be used for the calcining. Among these, fluidized bed calciners are preferably used.

[0029] The particle diameter of the fluid bed catalyst produced by these processes is in a range of 5-200 μm, and preferably in a range of 10-150 μm.

[0030] The catalyst produced by the present invention may be used for an ammoxidation of organic compounds. The organic compound used for an ammoxidation using the catalyst produced by the present invention includes, for

example, olefins, alcohols, ethers, aromatic compounds, heteroaromatic compounds, and the like. Specifically, the organic compound includes, for example, propylene, isobutene, methanol, ethanol, tert-butanol, methyl tert-butylether, toluene, xylene, picoline, quinaldine, and the like. In partictuar, if the catalyst produced by the present invention is used for an ammoxidation of propylene, isobutene, methanol, and tert-butanol, preferable results are obtained.

[0031] In general, the ammoxidation is carried out under conditions in which the molar ratio between the raw organic compound/ ammonia/ air is 1/ 0.9-3/ 8-12, and reaction temperature is in a range of 370-500°C, and reaction pressure is in a range of normal pressure to 500 kPa. Apparent contact time is in a range of 0.1-20 seconds. Air is conveniently used as an oxygen source, but air, which is diluted with water vapor, nitrogen, carbon dioxide gas, saturated hydrocarbons, and the like, is also used. In addition, oxygen enriched air is also used.

[0032] When the fluid bed catalyst having a stable catalytic structure, which is produced by the present invention, is successively used for the ammoxidation, the molybdenum component is dispersed, and a yield of ammoxidation products decreases. The reaction temperature of the ammoxidation using the fluid bed catalyst exceeds 400°C. It is impossible to prevent the dispersion of molybdenum component during the ammoxidation reaction. As a method for maintaining the properties of a catalyst for a long time, a method in which a molybdenum component is added to the catalyst during reaction has been suggested in Examined Japanese Patent Application, Second Publication No. Sho 58-57422, DE 3,311,521-C2, and WO 97/33863.

[0033] In the present invention, in order to maintain high yield of ammoxidation products for a long time, it is preferable to add a molybdenum component during an ammoxidation reaction. The molybdenum component, which is added to the catalyst during reaction, includes, for example, metal molybdenum, molybdenum trioxide, molybdic acid, ammonium dimolybdate, ammonium paramolybdate, ammonium octamolybdate, ammonium dodecamolybdate, phosphomolybdic acid, and the like. These molybdenum components can be used as gas or liquid. However, in practice, the molybdenum component in a solid state is used. In addition, these molybdenum components may be supported with inactivated materials or the catalyst. In particular, a method, in which the molybdenum component is enriched in the catalyst, is effective. Since this method has excellent utilization efficiency, and prevent generation of the problems due to a deposition of molybdenum oxide in the reaction system, this method is preferable. A method for producing molybdenum enriched catalyst disclosed in Unexamined Japanese Patent Application, First Publication No. Hei 11-33400 and the like, can be adopted.

[0034] The molybdenum component is added successively or intermittently into a reactor. The timing of addition and the amount added may be determined depending on a reaction progress. However, the amount added of the molybdenum component at a time is preferably in a range of 0.05-2% by mass with respect to 100% by mass of the catalyst, which has already added. When an excess amount of the molybdenum component is added at a time, the molybdenum component is dispersed out of the reaction system, and this is wasted. In addition, an excess amount of the molybdenum component is deposited in the reactor, and this may lead to problems in operation of the reactor.

[0035] Below, the present invention will be explained with Examples and Comparative

Examples.

Catalyst Activity Test

[0036] A catalyst activity test was carried out utilizing an ammoxidation of propylene as follows. The results of the activity test are shown in Tables 1-3 and 1-4 below.

[0037] The catalyst was filled in a fluid bed reactor comprising a catalyst fluidized portion having an inner diameter of 25 mm and a height of 400 mm. After that, a mixture gas containing propylene, ammonia, air, and water vapor (mixing molar ratio of propylene/ ammonia/ air/ water vapor is 1/ 1.2/ 9.5/ 0.5) was introduced into the fluid bed reactor such that a gas linear velocity was 4.5 cm/sec. The reaction pressure was adjusted to 200 kPa.

[0038] During the reaction, a catalyst in which the molybdenum component was enriched, was added such that 0.1-0.2% by mass of molybdenum contained in the added catalyst with respect to 100% by mass of the filled catalyst was added at intervals of 100-500 hours.

Contact time (sec.) = Catalyst volume (ml) based on apparent bulk density / Gas flow rate (ml/ sec.) converted by reaction conditions

Yield (%) of acrylonitrile = Molar number of produced acrylonitrile / Molar number of supplied propylene X 100

Catalyst Strength Test

[0039] Strength of the catalyst particles produced in Examples and Comparative Examples was measured according to a method disclosed in Unexamined Japanese Patent Application, First Publication No. Hei 9-70542 as follows, and the strength of the catalyst particles are shown in Tables 1-3 and 1-4 below as a compressive strength (N/ particle).

Use device: Shimazu MCTM-200 (marketed by Shimazu Corporation)

Pressure element: upper pressure element, which is made of diamond and which has a flat end surface having a diameter of 500 μm, and lower pressure plate, which is made of SUS

Pressure ratio: 7.06 X 10^{-3} N/sec

Sample: catalyst having a particle diameter of 45-50 μm

[0040] The catalyst having a particle diameter of 45-50 μm was prepared by sieving using Micro-Mesh@ Precision Sieves marketed by Buckbee-Mears St. Paul Company. Thirty particles, which were randomly selected from particles having a diameter of 45-50 μm, were used as samples. The average compressive strength of the thirty particles was the compressive strength of the sample.

Example 1

[0041] A fluid bed catalyst of which the composition is represented by Mo10 Bi0.4 Fe1.2 Ni6.0 Ce0.3 Cr0.8 P0.1 B0.1 K0.2 Oi (SiO_2)35 (i, which is an atomic ratio of oxygen, is determined depending on a valence of other elements, and therefore, the atomic ratio of oxygen will be omitted below) was produced by the following processes.

[0042] 409.4 g of ammonium paramolybdate was dissolved in 300 g of pure water. After that, 2.7 g of 85%-phosphoric acid and 0.5 g of boric anhydride were further added. A solution, in which 45.0 g of bismuth nitrate, 4.7 g of potassium nitrate, 404.7 g of nickel nitrate, 74.2 g of chromium nitrate, 30.2 g of cerium nitrate, and 25.0 g of citric acid were added to 270 g of 3.3%-nitric acid, was mixed with the prepared solution. After that, 2438.6 g of 20%-silica sol was also added. A solution, in which 112.4 g of iron nitrate and 25.0 g of citric acid were dissolved in 270 g of pure water, was prepared, and this solution was also added. While the prepared slurry was stirred, 15%-aqueous ammonia was added to adjust the pH of the slurry to a pH of 2.0. The concentration of the slurry at this time was 21.1% by mass. This slurry was concentrated at 102°C for 7 hours such that the slurry concentration was 28.8% by mass.

[0043] The concentrated slurry was spray dried using a rotary-disc type spray dryer in that the inlet temperature was 330°C and the outlet temperature was 160°C. After dried particles were heat treated at 250°C for 2 hours and 400°C for 2 hours, and then these particles were finally calcined at 650°C for 3 hours.

Example 2

[0044] A fluid bed catalyst was prepared in a manner identical to that of Example 1. except that the composition of the prepared fluid bed catalyst was represented by Mo10 Bi0.5 Fe1.1 Ni4.0 Ce0.4 La0.2 Cr1.0 Co2.0 P0.2 B0.2 K0.2 Si35 and the prepared particles were calcined under conditions which are shown in Table 1-3. Moreover, nitrates of La and Co were used as a raw material of La and Co and they were added next to nickel nitrate.

Example 3

[0045] A fluid bed catalyst was prepared in a manner identical to that of Example 1, except that the composition of the prepared fluid bed catalyst was represented by Mo10 Bi0.5 Pe1.3 Ni5.0 Ce0.3 Cr0.6 Mg1.0 Zr0.2 K0.2 Si35 and the prepared particles were calcined under conditions which are shown in Table 1-3. Moreover, nitrates of Mg and Zr were used as a raw material of Mg and Zr and they were added next to nickel nitrate.

Example 4

[0046] A fluid bed catalyst was prepared in a manner identical to that of Example 1, except that the composition of the prepared fluid bed catalyst was represented by Mo10 Bi0.3 Fe1.1 Ni6.0 Ce0.2 Pr0.1 Cr0.8 Zn0.2 P0.3 K0.1 Rb0.1 Si40 and the prepared particles were calcined under conditions which are shown in Table 1-3. Moreover, nitrates of Pr, Zn and Rb were used as a raw material of Pr, Zn, and Rb and they were added next to nickel nitrate.

Example 5

[0047] A fluid bed catalyst was prepared in a manner identical to that of Example 1, except that the composition of the prepared fluid bed catalyst was represented by Mo10 Bi0.4 Fe0.9 N15.5 Ce0.4 Cr1.2 Mn0.4 W0.4 Pd0.01 P0.2 B0.2 K0.2 Si35 and the prepared particles were calcined under conditions which are shown in Table 1-3. Moreover,

nitrates of Mn and Pd were used as a raw material of Mn and Pd and they were added next to nickel nitrate. Ammonium paratungstate was used as a raw material of W and this was added next to ammonium paramolybdate.

Example 6

[0048] A fluid bed catalyst the composition of which is represented by Mo10 Bi0.4 Fe1.2 Ni6.0 (FeSb1.1)3 Ce0.3 Cr0.8 P0.1 B0.1 K0.2 Si35, was produced by the following processes.

[0049] 348.9 g of ammonium paramolybdate was dissolved in 300 g of pure water. After that, 2.3 g of 85%-phosphoric acid and 0.4 g of boric anhydride were further added. A solution, in which 38.4 g of bismuth nitrate, 4.0 g of potassium nitrate, 344.9 g of nickel nitrate, 63.3 g of chromium nitrate, 25.7 g of cerium nitrate, and 25.0 g of citric acid were added to 270 g of 3.3%-nitric acid, was mixed with the prepared solution. After that, 2078.6 g of 20%-silica sol was also added. A solution, in which 95.8 g of iron nitrate and 25.0 g of citric acid were dissolved in 270 g of pure water, was prepared, and this solution was also added. While the prepared slurry was stirred, 15%-aqueous ammonia was added to adjust the pH of the slurry to a pH of 2.3. The concentration of the slurry at this time was 21.1% by mass. This slurry was concentrated at 102°C for 7 hours such that the slurry concentration was 28.8% by mass. After that, 369.1 g of 40%-iron antimonate slurry was added.

[0050] The concentrated slurry was spray dried using a rotary-disc type spray dryer, and the inlet temperature was 330°C and the outlet temperature was 160°C. After dried particles were heat treated at 250°C for 2 hours and 400°C for 2 hours, these particles were finally calcined at 650°C for 3 hours.

Example 7

[0051] A fluid bed catalyst of which the composition is identical to the composition of the fluid bed catalyst of Example 3 was produced by the following processes.

[0052] 409.8 g of ammonium paramolybdate was dissolved in 2,000 g of pure water. A solution, in which 56.3 g of bismuth nitrate, 4.7 g of potassium nitrate, 337.6 g of nickel nitrate, 55.7 g of chromium nitrate, 30.2 g of cerium nitrate, 59.5 g of magnesium nitrate, 12.4 g of zirconium nitrate, and 25.0 g of citric acid were added to 270 g of 3.3%-nitric acid, was mixed to the prepared solution. After that, 2441.0 g of 20%-silica sol was also added. A solution, in which 121.9 g of iron nitrate and 25.0 g of citric acid were dissolved in 270 g of pure water, was prepared, and this solution was also added. While the prepared slurry was stirred, 15%-aqueous ammonia was added to adjust the pH of the slurry to a pH of 2. The concentration of the slurry at this time was 14.7% by mass. This slurry was concentrated at 102°C for 2 hours such that the slurry concentration was 21.1% by mass.

[0053] The concentrated slurry was spray dried using a rotary-disc type spray dryer, and the inlet temperature was 330°C and the outlet temperature was 160°C. After dried particles were heat treated at 250°C for 2 hours and 400°C for 2 hours, these particles were finally calcined at 650°C for 3 hours.

Example 8

[0054] A fluid bed catalyst of which the composition is identical to the composition of the fluid bed catalyst of Example 1 was produced by the following processes.

[0055] 409.4 g of ammonium paramolybdate was dissolved in 3,000 g of pure water. After that, 2.7 g of 85%-phosphoric acid and 0.5 g of boric anhydride were further added. A solution, in which 45.0 g of bismuth nitrate, 4.7 g of potassium nitrate, 404.7 g of nickel nitrate, 74.2 g of chromium nitrate, 30.2 g of cerium nitrate, and 25.0 g of citric acid were added to 270 g of 3.3%-nitric acid, was mixed to the prepared solution. After that, 2438.6 g of 20%-silica sol was also added. While the prepared slurry was stirred, 15%-aqueous ammonia was added to adjust the pH of the slurry to a pH of 5.0. This slurry was heated at 99°C for 1.5 hours. A solution, in which 112.4 g of iron nitrate and 25.0 g of citric acid were dissolved in 270 g of pure water, was prepared, and this solution was also added. The concentration of the slurry at this time was 13.0% by mass and the pH thereof was 4.8. This slurry was concentrated at 102°C for 4 hours such that the slurry concentration was 22.4% by mass.

[0056] The concentrated slurry was spray dried using a rotary-disc type spray dryer, and the inlet temperature was 330°C and the outlet temperature was 160°C. After dried particles were heat treated at 250°C for 2 hours and 400°C for 2 hours, these particles were finally calcined at 640°C for 3 hours.

Example 9

[0057] A fluid bed catalyst of which the composition is represented by Mo10 Bi0.6 Fe0.7 Ni7.0 (FeSb1.1)4.5 Ce0.5 P0.2 B0.2 Te0.25 K0.6 Si 40 was produced by the following processes.

[0058] 180.6 g of ammonium paramolybdate was dissolved in 1,200 g of pure water. After that, 3.9 g of 85%-phos-

phoric acid and 2049.1 g of 20%-silica sol were further added, in that order. A solution, in which 347.1 g of nickel nitrate, 37.0 g of cerium nitrate, 10.3 g of potassium nitrate, 25 g of citric acid, and 49.6 g of bismuth nitrate were added to 270 g of 3.3%-nitric acid, was mixed with the prepared solution. While the prepared slurry was stirred, 15%-aqueous ammonia was added to adjust the pH of the slurry to a pH of 7.7. Then, the slurry was subjected to a heat treatment in which the slurry was refluxed at 99°C for 1.5 hours.

[0059] 5.4 g of metal tellurium, 4.5 g of ammonium paramolybdate, and 20 g of hydrogen peroxide were added to 250 g of water, and these were dissolved in water by stirring at 95-100°C. This prepared solution was cooled to room temperature and 25 g of citric acid and 48.2 g of iron nitrate were dissolved in the solution. While the prepared solution was stirred, 15%-aqueous ammonia was added to adjust the pH of the slurry to a pH of 9.2. 115.9 g of ammonium paramolybdate was added little by little and dissolved in the solution. After that, the pH of the solution was adjusted to 7 by adding aqueous ammonia.

[0060] This solution was mixed in the prepared slurry, and 480.8 g of 40%-iron antimonate slurry was further added. The concentration of the slurry at this time was 13.8% by mass and the pH thereof was 7.2. This slurry was concentrated at 102°C for 5.5 hours such that the slurry concentration was 17.2% by mass.

[0061] The concentrated slurry was spray dried using a rotary-disc type spray dryer, and the inlet temperature was 330°C and the outlet temperature was 160°C. After dried particles were heat treated at 250°C for 2 hours and 400°C for 2 hours, these particles were finally calcined at 580°C for 3 hours.

Example 10

[0062] A fluid bed catalyst of which the composition is identical to the composition of the fluid bed catalyst of Example 1 was produced by the following processes.

[0063] 409.4 g of ammonium paramolybdate was dissolved in 3,000 g of pure water. After that, 2.7 g of 85%-phosphoric acid and 0.5 g of boric anhydride were further added. A solution, in which 45.0 g of bismuth nitrate, 4.7 g of potassium nitrate, 404.7 g of nickel nitrate, 74.2 g of chromium nitrate, 30.2 g of cerium nitrate, and 25.0 g of citric acid were added to 270 g of 3.3%-nitric acid, was mixed with the prepared solution. After that, 2438.6 g of 20%-silica sol were further added. Another solution, in which 112.4 g of iron nitrate and 25.0 g of citric acid were dissolved in 270 g of pure water, was prepared, and this solution was also added. While the prepared slurry was stirred, 15%-aqueous ammonia was added to adjust the pH of the slurry to a pH of 3.0. This slurry was heated at 99°C for 1.5 hours. The concentration of the slurry at this time was 12.5% by mass. This slurry was concentrated at 102°C for 4 hours such that the slurry concentration was 22.1% by mass.

[0064] The concentrated slurry was spray dried using a rotary-disc type spray dryer, and the inlet temperature was 330°C and the outlet temperature was 160°C. After dried particles were heat treated at 250°C for 2 hours and 400°C for 2 hours, these particles were finally calcined at 650°C for 3 hours.

Comparative Example 1

[0065] A comparative fluid bed catalyst was prepared in a manner identical to that of Example 1, except that the concentration treatment for 7 hours was not carried out and the prepared particles were calcined under conditions which are shown in Table 1-4.

Comparative Example 2

[0066] A comparative fluid bed catalyst having a composition identical to that of Example 3 was prepared in a manner identical to that of Example 7, except heat treatment at 99°C for 2 hours was carried out instead of concentration treatment and the prepared particles were calcined under conditions which are shown in Table 1-4.

Comparative Example 3

[0067] A comparative fluid bed catalyst having a composition identical to that of Example 6 was prepared in a manner identical to that of Example 6, except that the concentration treatment for 7 hours was not carried out and the prepared particles were calcined under conditions which are shown in Table 1-4.

Comparative Example 4

[0068] A comparative fluid bed catalyst having a composition identical to that of Example 1 was prepared in a manner identical to that of Example 8, except that the solution containing iron nitrate and citric acid was added to the slurry after the concentration treatment and the prepared particles were calcined under conditions which are shown in Table

1-4.

[0069] The ammoxidation of propylene was carried out under conditions explained above using the catalysts prepared in Examples and Comparative Examples.

[0070] The results are shown in Tables below.

Table 1-1

		Mo	Bi	Fe	Ni	FeSb		F	G	H	M	X	Y	SiO_2
						Fe	Sb							
Example	1	10	0.4	1.2	6.0			Ce 0.3	Cr 0.8			P 0.1 B 0.1	K 0.2	35
	2	10	0.5	1.1	4.0			Ce 0.4 La 0.2	Cr 1.0 Co 2.0			P 0.2 B 0.2	K 0.2	35
	3	10	0.5	1.3	5.0			Ce 0.3	Cr 0.6 Mg 1.0	Zr 0.2			K 0.2	35
	4	10	0.3	1.1	6.0			Ce 0.2 Pr 0.1	Cr 0.8 Zn 0.2			P 0.3	K 0.1 Rb 0.1	40
	5	10	0.4	0.9	5.5			Ce 0.4	Cr 1.2 Mn 0.4	W 0.4	Pd 0.01	P 0.2 B 0.2	K 0.2	35
	6	10	0.4	1.2	6.0	3.0	3.3	Ce 0.3	Cr 0.8			P 0.1 B 0.1	K 0.2	35
	7	10	0.5	1.3	5.0			Ce 0.3	Cr 0.6 Mg 1.0	Zr 0.2			K 0.2	35
	8	10	0.4	1.2	6.0			Ce 0.3	Cr 0.8			P 0.1 B 0.1	K 0.2	35
	9	10	0.6	0.7	7.0	4.5	5	Ce 0.5				P 0.2 B 0.2 Te 0.25	K 0.6	40
	10	10	0.4	1.2	6.0			Ce 0.3	Cr 0.8			P 0.1 B 0.1	K 0.2	35

Table 1-2

		Mo	Bi	Fe	Ni	FeSb		F	G	H	M	X	Y	SiO_2
						Fe	Sb							
Comparative Example	1	10	0.4	1.2	6.0			Ce 0.3	Cr 0.8			P 0.1 B 0.1	K 0.2	35
	2	10	0.5	1.3	5.0			Ce 0.3	Cr 0.6 Mg 1.0	Zr 0.2			K 0.2	35
	3	10	0.4	1.2	6.0	3.0	3.3	Ce 0.3	Cr 0.8			P 0.1 B 0.1	K 0.2	35
	4	10	0.4	1.2	6.0			Ce 0.3	Cr 0.8			P 0.1 B 0.1	K 0.2	35

Table 1-3

Examples	Concentration Treatment				Burning temperature [°C]	Contact time [sec.]	Yield of acrylonitrile [%] Progress time [hour]			Compressive strength X 10^{-3} [N/particle]
	pH before concentration treatment	Concentration before concentration treatment [%]	Concentration after concentration treatment [%]	Concentration treatment time [hours]			50	500	1,000	
1	2.2	21.1	28.8	7.0	650	2.4	82.9	82.9	83.0	150
2	2.5	21.1	28.7	7.0	650	2.3	82.6	82.6	82.5	150
3	2.3	21.0	28.6	7.0	640	2.4	82.8	82.6	82.7	135
4	1.8	21.1	28.7	7.0	660	2.1	82.5	82.6	82.5	140
5	2.0	21.0	28.7	7.0	650	2.3	82.6	82.4	82.3	145
6	2.3	21.1	28.7	7.0	650	2.2	83.1	83.0	83.1	160
7	2.0	14.7	21.1	2.0	640	2.7	82.5	82.3	82.3	120
8	2.3	12.6	22.0	4.0	640	2.3	82.8	82.6	82.6	155
9	7.2	13.8	17.2	5.5	580	2.3	83.1	82.9	82.7	195
10	3.0	12.5	22.1	4.0	650	2.4	82.7	82.6	82.6	145

Table 1-4

		Concentration Treatment				Burning temperature [°C]	Contact time [sec.]	Yield of acrylonitrile [%]			Compressive strength X 10^{-3} [N/particle]
								Progress time [hour]			
		pH before concentration treatment	Concentration before concentration treatment [%]	Concentration after concentration treatment [%]	Concentration treatment time [hours]			50	500	1,000	
Comparative Examples	1	-	no concentration 21.1	no concentration 21.1	0.0	630	3.3	81.6	81.4	81.1	80
	2	-	no concentration 14.7	no concentration 14.7	heating 2.0	640	3.1	81.5	81.5	81.3	100
	3	-	no concentration 21.1	no concentration 21.1	0.0	630	2.5	82.0	81.7	81.6	85
	4	4.8	13.0	22.4	4.0	640	2.4	81.8	81.7	81.8	90

INDUSTRIAL APPLICABILITY

[0071] The production method of the present invention can yield a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst with an excellent reproducibility. The molybdenum-bismuth-iron containing composite oxide fluid bed catalyst produced by the present invention has a high activity and this yields the target ammoxidation product at high yield. For example, by using the molybdenum-bismuth-iron containing composite oxide fluid bed catalyst produced by the present invention in an ammoxidation of propylene, acrylonitrile can be obtained at high yield.

Claims

1. A method for producing a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst which is a method for producing a composite oxide catalyst containing components (1) molybdenum, (2) bismuth, (3) iron, (4) nickel, (5) at least one element selected from lithium, sodium, potassium, rubidium, cesium and thallium, and (6) silica, as essential components, wherein a slurry containing at least components (1), (2), (3), and (6) is concentrated in a range of 50-120°C, so that the concentration difference of the slurry between before and after the concentration treatment is in a range of 2-15% by mass.

2. A method for producing a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst according to claim 1, wherein the concentration of the slurry after the concentration treatment is in a range of 15-35% by mass.

3. A method for producing a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst according to claim 1 or 2, wherein the pH of the slurry before the concentration treatment is adjusted in a range of 1-4.

4. A method for producing a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst according to one of claims I to 3, wherein the composite oxide fluid bed catalyst has a composition represented by

$$Mo10\ Bia\ Feb\ Nic\ (Fe\ Sbd)e\ Ff\ Gg\ Hh\ Mm\ Xx\ Yy\ Oi(SiO_2)j$$

in the formula, Mo, Bi, Fe, Ni, and (FeSbd) denote molybdenum, bismuth, iron, nickel and iron antimonate; F denotes at least one element selected from yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, aluminum. and gallium; G denotes at least one element selected from magnesium, calcium, strontium, barium, chromium, manganese, cobalt, copper, zinc, and cadmium; H denotes at least one element selected from titanium, zirconium, vanadium, niobium, tantalum, tungsten, germanium, tin, lead, and antimony; M denotes at least one element selected from ruthenium, rhodium, palladium, rhenium, osmium, iridium, platinum, and silver; X denotes at least one element selected from boron, phosphorus, and tellurium; Y denotes at least one element selected from lithium, sodium, potassium, rubidium, cesium, and thallium; O denotes oxygen; SiO_2 denotes silica; symbols a, b, c, d, e, f, g, h, m, x, y, i, and j denote atomic ratio; when the atomic ratio of Mo is 10, a is in a range of 0.2-1.5, b is in a range of 0.7-15, c is in a range of 3-12, d is in a range of 0.8-2, e is in a range of 0-20, f is in a range of 0.1-1.5, g is in a range of 0-5, h is in a range of 0-3, m is in a range of 0-1.0, x is in a range of 0-3, y is in a range of 0.05-1.5, i is the number of oxygen elements in metal oxides, which are formed by combining these elements; and j is in a range of 20-200.

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[7] B01J23/88, C07C253/26, 255/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl[7] B01J21/00-37/36

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926-1996	Toroku Jitsuyo Shinan Koho	1994-2002
Kokai Jitsuyo Shinan Koho	1971-2002	Jitsuyo Shinan Toroku Koho	1996-2002

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E,X	JP 2001-187772 A (Mitsubishi Rayon Co., Ltd.), 10 July, 2001 (10.07.01), Claim 1; example 1 (Family: none)	1-4
X A	JP 63-250357 A (Nitto Chemical Industry Co., Ltd.), 18 October, 1988 (18.10.88), Claims; page 4, lower left column, lines 3 to 8; example 1 (Family: none)	1-3 4
X A	EP 340909 A1 (Nitto Chemical Industry Co., Ltd.), 08 November, 1989 (08.11.89), Claims; examples & US 5158787 A & JP 1-257125 A	1-2 3-4

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"&" document member of the same patent family

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